

Catalytic dechlorination of gas-phase perchloroethylene under mixed redox conditions

Özer Orbay^a, Song Gao^{b,*}, Brian Barbaris^b, Erik Rupp^a, A. Eduardo Sáez^a,
Robert G. Arnold^a, Eric A. Betterton^b

^aDepartment of Chemical and Environmental Engineering, The University of Arizona, Tucson, AZ 85721, United States

^bDepartment of Atmospheric Sciences, The University of Arizona, Tucson, AZ 85721, United States

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Abstract

The validity of a new method to destroy gas-phase perchloroethylene (PCE) is demonstrated at bench scale using a fixed-bed reactor that contains a Pt/Rh catalyst. Hydrogen and oxygen were simultaneously fed to the reactor together with PCE. The conversion efficiencies of PCE were sensitive to H₂/O₂ ratio and reactor temperature. When the temperature was ≥ 400 °C and H₂/O₂ was ≥ 2.15 , PCE conversion efficiency was maintained at $\geq 90\%$. No catalyst deactivation was observed for over 2 years, using only mild, convenient regeneration procedures. It is likely that PCE reduction steps precede oxidation reactions and that the importance of oxidation lies in its elimination of intermediates that would otherwise lead to catalyst poisoning. In practice, this catalytic dechlorination method holds potential for low-cost, large-scale field operation.

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1. Introduction

Acyclic, short-chain halogenated organics are useful solvents, the principal representatives being tetrachloroethylene (PCE), trichloroethylene (TCE) and methylene chloride. Because of their widespread use such as in dry cleaning and metal degreasing, chlorinated compounds are found at thousands of contaminated sites in the United States. In particular, PCE and TCE are among the top 31 Priority Hazardous Substances that are determined to pose the most significant potential threat to human health by the Department of Health and Human Services (DHHS) [1,2]. A recent nationwide study [1] ranks PCE and TCE as the first and third most frequently detected solvents in ground water at concentrations greater than their respective Maximum Contaminant Levels (MCLs) [3]. The same study indicates that PCE and TCE comprise the most frequently occurring mixture of solvents in ground water. Alarming, both PCE

and TCE are reasonably anticipated to be human and animal carcinogens according to the DHHS and several research institutions [2]. There is thus substantial interest in the development of efficient, economic methods for remediating ground water and soils contaminated with halogenated organic solvents.

At U.S. Superfund sites, incineration and solidification have been traditionally employed as remediation technologies to treat chlorinated solvents. More recently, soil vapor extraction (SVE) and pump-and-treat methods have been used at many Superfund sites [4]. However, all of these technologies can be expensive. In addition, they can lead to other environmental problems (such as air pollution in the case of incineration) or they merely separate contaminants into a different phase rather than destroy them. Abiotic transformations, such as reduction and oxidation reactions, are the most studied alternatives to separation technologies for treatment of chlorinated solvents. The method of choice depends mainly on the nature of the carbon–halogen and carbon–carbon bonds in the target molecule [5]. A variety of metals have been used to catalyze the destruction of halogenated solvents under either oxidizing or reducing condition.

* Corresponding author. Tel.: +1 520 626 3552.

E-mail address: songatmo@email.arizona.edu (S. Gao).

1.1. Catalytic oxidation reactions

Catalyzed oxidative dehalogenation occurs when an organochlorine compound is oxidized to CO₂ in the presence of oxygen. Upon oxidation, chlorinated VOCs yield HCl in addition to CO₂ and H₂O. Formation of incomplete oxidation products such as dioxins and furans is an important consideration due to their toxicity. In addition, formation of Cl₂ has been observed, such as in the catalytic oxidation of CH₃Cl over α-Cr₂O₃/Al₂O₃ [6] and in the oxidation of TCE and 1,1-dichloroethylene over a similar catalyst [7].

Commercially available catalysts fall into three broad categories: base metal oxides (e.g. Cu, Cr, and Mn); supported noble metal catalysts (e.g. Pt, Pd); and noble metal/metal oxide combinations [8–12]. Detailed kinetics of catalytic oxidation on noble metals is not firmly established, but may follow either a Langmuir–Hinshelwood type of mechanism (reaction between adsorbed oxygen and an adsorbed reactant) or an Eley–Rideal mechanism (reaction between adsorbed oxygen and a gas-phase reactant molecule) [13]. Platinum on various oxide supports is commonly used to catalyze oxidative dehalogenation reactions. Unfortunately, Pt is typically poisoned by chlorinated compounds, so deactivation is an important performance characteristic. Deactivation can be minimized by controlling the state and loading of Pt in the catalyst [9,14] or choosing an appropriate temperature range [15,16].

Since some chlorinated hydrocarbon molecules contain more chlorine than hydrogen atoms, some research has focused on methods for providing hydrogen in order to convert all the chlorine to hydrogen chloride (HCl) and prevent the accumulation of unwanted products [9–11,17,18]. Hexane, water and toluene [11]; methane and water [10,17]; and propane [9] have been studied as the hydrogen source. Gonzalez-Velasco et al. [11] observed that complete catalytic oxidation of TCE over alumina-supported Pt or Pd occurred at an accelerated rate in the presence of hexane or toluene. Water did not alter the catalytic activity of the Pd catalyst, while TCE oxidation on the Pt catalyst was enhanced by water vapor at low temperatures (<400 °C) but inhibited at higher ones. Production of HCl was improved for both catalysts by adding a hydrogen source. There have been several successful field applications of catalytic oxidation for the destruction of VOCs, although relatively little of this work is described in the literature [19–21].

1.2. Catalytic hydrodechlorination reactions

In catalytic hydrodechlorination, halogenated compounds are commonly reduced to corresponding hydrocarbons on a catalyst surface using H₂ as the reducing agent,



Table 1
Previous investigations of catalytic hydrodechlorination

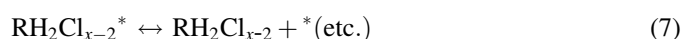
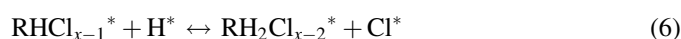
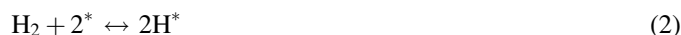
Catalysts	Reactants	References
NiMo/Al ₂ O ₃ (sulfided)	Chlorinated benzenes	[22]
NiMo/Al ₂ O ₃ (sulfided)	Chloropyridinols	[23]
Ni/Mo-γ-alumina (sulfided)	Dichloromethane, 1,1,1-TCA, TCE, PCE	[24]
Pd/C (w/sodium hypophosphite)	1,2,4,5-Tetrachlorobenzene	[25]
Nickel loaded silica and exchanged Y-zeolite	Chlorophenols, dichlorophenols, trichlorophenols, pentachlorophenol	[26]
Pd/Al ₂ O ₃ , Rh/Al ₂ O ₃	Chlorobenzene	[27]
Pt/C, Pd/γ-Al ₂ O ₃	4-Chloro-2-nitrophenol	[28]
Rh/SiO ₂	Dichloroethane (DCA), TCE	[29]
Pt/Al ₂ O ₃	Dichloroethylene (DCE)	[30,31]
Pd on carbon	Chlorofluorocarbons	[32]
Pt on various support,	Carbon tetrachloride (CCl ₄)	[33]
Pt/γ-Al ₂ O ₃	Carbon tetrachloride	[34]
Pt/MgO	Carbon tetrachloride	[35]
Pd oxide on γ-Al ₂ O ₃	1,1,2-Trichlorotrifluoroethane	[36]
Ni on Y zeolites	Carbon tetrachloride	[37]
Pd–Cu–Sn on carbon	PCE	[38]
Pt–Cu–Ag–Au on carbon	1,2-Dichloropropane	[39]
Ni on ZSM-5 and Al ₂ O ₃	TCE and TCA	[40]
Pd on carbon	Aqueous TCE, TCA, and chlorobenzene	[41]
Pd on Al ₂ O ₃ , fluorinated Al ₂ O ₃ and AlF ₃	1,1-Dichlorotetrafluoroethane, dichlorodifluoromethane	[42]
Group VIII noble metals	Dichlorodifluoromethane	[43]
Pd, Rh, Pt, on alumina	PCE	[44]
Pd on silica	1,1,1-Trichloroethane (TCA)	[45]
NiMo/Al ₂ O ₃	PCE, TCE, 1,1-dichloroethylene, <i>cis</i> -dichloroethylene and <i>trans</i> -dichloroethylene	[46]
Pd/γ-Al ₂ O ₃	CF ₂ -Cl ₂ (CFC-12)	[47]
Ni-Raney, Ni on SiO ₂ , Pd/Al ₂ O ₃ , Pt/Al ₂ O ₃ , Pt/Rh/Al ₂ O ₃ , Ru/Al ₂ O ₃ and sulfided Ni–Mo on Al ₂ O ₃	Dichloromethane, chloroform, carbon tetrachloride, 1,1,1-TCA, TCE and PCE	[48]
Pt on various alumina supports	TCA	[49]
Pt and Pd on Vycor, Al ₂ O ₃ , C, AlF ₃ ,	Chloromethanes, chlorobenzene	[50]

Hydrodechlorination (HDC) has the following advantages over incineration and oxidation: (i) reaction products include primarily HCl, which can be easily separated by caustic washing, and hydrocarbons, which can be safely burned. Incineration products, on the other hand, may contain highly toxic compounds such as chlorine, phosgene, and dioxins; (ii) HDC reactions can destroy a variety of halogenated organic compounds; (iii) reaction rates are typically fast; (iv) transformation conditions (temperature and pressure) are typically mild; (v) there is no NO_x formation due to relatively low reaction temperatures; and (vi) the process can be economically attractive.

Research on catalytic HDC has focused on catalyst screening and its applicability to different types of halogenated organic compounds. The variety of catalysts investigated includes supported and unsupported precious metals. Halogenated target contaminants include chlorofluorocarbons, chlorinated aromatics and chlorinated aliphatics in organic matrices, aqueous and gas phases. A detailed summary is provided in Table 1. Complete dechlorination is generally achieved. In addition to molecular hydrogen, alcohols, formates and some hydrocarbons have been investigated as potential hydrogen donors, although to a lesser extent [51].

Loss of catalyst activity over time is common in catalytic HDC. Since the most effective catalysts so far studied are supported precious metals such as Pt and Pd, catalyst lifetime has a great effect on process economics and feasibility. Despite considerable study, the mechanisms of catalyst deactivation and methods for catalyst regeneration are not well established. Deactivation is frequently attributed to chlorine poisoning or coking on the catalyst surface. Although less common, catalyst sintering and leaching of metal from support material have also been observed.

In the literature, two major reaction mechanisms are postulated for HDC reactions [32,52]: a sequential/serial mechanism and a concerted/parallel mechanism. A sequential mechanism can be represented as follows:



where (*) refers to an active site on the catalytic surface or an adsorbed species that is activated. Reaction (4) (and (6), etc.), the surface reaction between adsorbed RCl_x and adsorbed atomic hydrogen, is believed to be the rate-determining step (RDS), which involves scission of the C–Cl bond. Anticipated reaction rates are a function of the C–Cl bond strength in respective organochlorine target molecules. A sequential mechanism characteristically involves desorption (such as

Reactions (5) and (7)) and re-adsorption (such as Reaction (3)) of chlorinated intermediates. On the other hand, a concerted reaction mechanism refers to the removal of multiple chlorines without desorption of partially chlorinated intermediates, which can be represented by:



The concerted multi-chlorine removal mechanism would mainly produce fully dechlorinated hydrocarbons. However, simultaneous formation of fully dechlorinated products and partially chlorinated intermediates is frequently observed. Parallel reaction pathways are frequently proposed to explain this observation. Here, the heavily chlorinated parent compounds are transformed to less chlorinated compounds and completely dechlorinated hydrocarbons via different pathways that may compete for a common intermediate at branch points within the overall mechanism. Hypothetically, the relative contributions of each pathway are reflected in the product distribution and process kinetics, influencing the overall success of the remediation effort.

Unsaturated molecules are easily adsorbed and hydrogenated on the catalyst surface [30]. For chlorinated alkenes, both hydrogenation of C=C bonds and hydrogenolysis of C–Cl bonds can occur. Ordóñez et al. [48] suggested a mechanism in which the hydrogenation of double bonds takes place catalytically, while the elimination of HCl is essentially non-catalytic. Similar mechanisms have been suggested in aqueous solutions for various chlorinated and fluorinated alkenes [53,54].

Weiss and Krieger [30] proposed that the HDC of *cis*- and *trans*-1, 2-dichloroethylene (1,2-DCE) proceeds mainly by sequential removal of chlorines until eventually forming ethane, which is consistent with the observation of vinyl chloride (VC) as an intermediate product. They further suggested that both adsorption and hydrodechlorination are favored when more chlorine atoms are linked to the olefinic bond. However, the predominantly sequential mechanism does not appear to directly explain the product distribution obtained during the HDC of PCE and TCE by others [24,48,53], in which no chlorinated intermediates (such as VC) were detected.

Kim and Allen [46] proposed a reaction network for PCE that incorporates both sequential and concerted mechanisms. They concluded that the HDC of chlorinated olefins proceeds mainly through steps that involve the removal of multiple chlorine atoms without desorption of reaction intermediates, a concerted mechanism. In contrast, the HDC of chlorinated aromatics proceeds mainly through sequential removal of chlorine atoms with desorption of partially chlorinated intermediates.

Previous work on catalytic destruction of chlorinated hydrocarbons has focused on the study of either reduction or oxidation as the main mechanism. Reduction studies show high conversions at temperatures that are lower than those required by oxidation, albeit with relatively rapid catalyst deactivation mainly due to coking [49]. Simultaneous presence of oxygen and a hydrogen source might alter reaction mechanisms and kinetics of dechlorination. For example, Gervasini et al. [55]

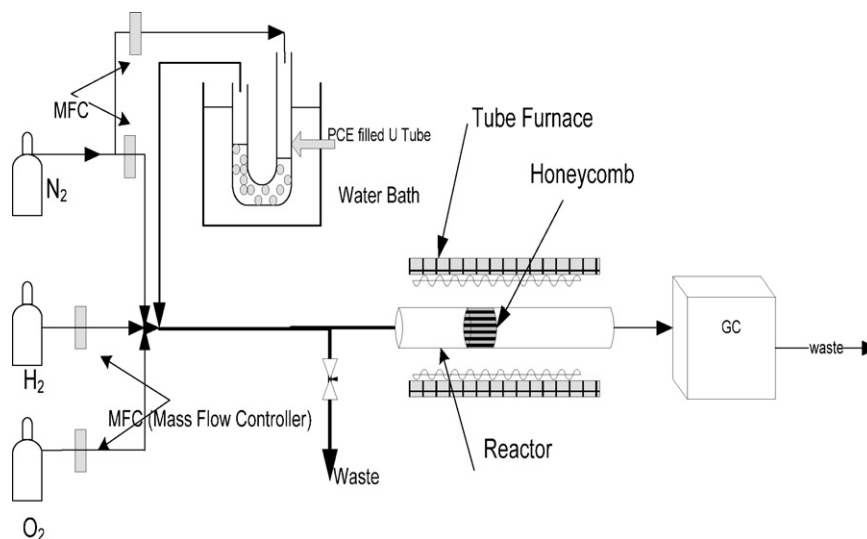


Fig. 1. Experimental setup for the dechlorination of PCE.

studied the oxidation of CCl_4 over a MnO_2 catalyst in the presence of CH_4 . They observed that, even though the addition of methane did not increase CCl_4 conversion, it increased the yield of HCl with respect to CO_2 . In this study, both H_2 and O_2 are added to the reaction system, which creates a mixed (i.e., simultaneous reducing and oxidizing) reaction environment (correspondingly termed “redox conditions”) for the conversion of PCE. The main hypothesis is that high conversions can be obtained at relatively low temperatures mainly through the reductive dehalogenation path, while at the same time the presence of oxygen can increase catalyst stability by preventing irreversible adsorption of by-products and formation of coke.

2. Experimental

2.1. Catalyst

The catalyst was originally manufactured for use in an automobile catalytic converter. Pt and Rh are supported, in a 3:1 (w/w) ratio, on a monolithic honeycomb (62 cells/ cm^2) that is composed of cordierite (90%) and washcoat (10%) containing alumina, cerium, zirconium and other trace constituents. The nominal loading is 1.85×10^{-4} g total metal/ cm^3 , where the volume is the total nominal envelope of the catalyst (uncut block was 820 cm^3). Cylindrical pieces (2.54 cm diameter \times 2.54 cm long) were cut from honeycomb blocks and used in the tube reactor described below. Each channel in the block has a square cross section with dimensions $2 \text{ mm} \times 2 \text{ mm}$.

A series of control experiments were performed to establish the reactivity of the alumina honeycomb support. The unamended alumina support, or monolithic honeycomb, is commercially available (Applied Ceramics, Inc., Doraville, Georgia). Experiments on PCE destruction under typical operating conditions used in this work showed insignificant PCE conversion.

2.2. Reactor system

Experiments were carried out in a fixed-bed tubular reactor (Fig. 1). The reactor is a 50 cm (long) \times 2.54 cm (inner diameter) glass tube (ACE Glassware), containing a 2.54 cm (long) \times 2.54 cm (outer diameter) honeycomb cylinder. The tubular reactor was housed in a vertically aligned, single-zone tube furnace (Thermolyne 21100), equipped with automatic control of the temperature that could be ramped at desired rates. The length of the furnace was 38 cm. The honeycomb was located inside the reactor tube at a distance of approximately 20 cm from the upstream end of the furnace. This gives the gas in the tube enough residence time to warm up to the furnace temperature before it enters the honeycomb structure. Temperature was measured in two places using *K* type thermocouples (Omega Engineering): at the center of the inlet face of the honeycomb (the thermocouple was directly in contact with the solid surface of the honeycomb) and at the furnace inner wall above the honeycomb (set point for temperature control). Gas temperatures were not measured systematically since an independent measurement verified that the gas temperature at the entrance of the honeycomb block is approximately equal to the furnace temperature at the gas flow rates employed in this work.

A well-mixed gaseous stream consisting of H_2 , O_2 , N_2 , and PCE was fed to the reactor. Hydrogen (99.95%, Air Liquide), oxygen (99.9%, Air Liquide) and nitrogen (99.99%, The University of Arizona Cryogenics & Gas Facility) were used as obtained. Flows were regulated by Aalborg (Orangeburg, New York) mass flow controllers. Liquid PCE (Aldrich, 99.9+%) was placed in a U-tube located in a temperature-regulated water bath (4°C). Nitrogen (20 mL/min) was bubbled through the PCE, resulting in a PCE-loaded N_2 stream, which was then mixed with H_2 , O_2 and N_2 at desired ratios to obtain a total flow rate of 500 mL/min at room (i.e., ambient) temperature. Typical residence times ranged from 1.5 s (catalyst at room temperature) to 0.7 s (catalyst at

400 °C). A typical concentration of PCE in the influent gas stream was 800 ppmv.

2.3. Analytical

An HP 5890 gas chromatograph equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID) was used to analyze the influent and effluent streams. Gas samples were injected to the GC through Cheminert six-way slider injection valves (402 µL sample loop for TCD; 500 µL for FID) from Valco Instruments Co. Helium was used as the carrier gas. A 0.53-µm wide-bore capillary column (J&W DB-624, 30 m × 0.53 mm × 3.0 µm) with FID was used to measure dechlorinated and chlorinated hydrocarbons. For CO₂, H₂, and O₂ measurements, a Supleco packed column (60/80 mesh Carboxen-1000, 457 cm × 0.3175 mm × 2.1 mm, stainless steel) was used with TCD. The temperatures of the injector and the detectors were typically 200 °C and 250 °C, respectively.

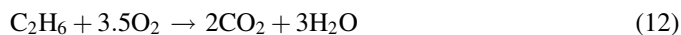
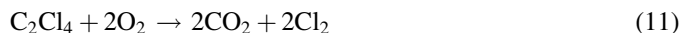
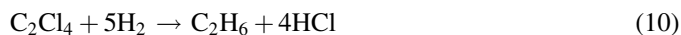
2.4. Experiments

In a typical experiment, the initial furnace temperature was 75 °C. The influent gas stream was diverted to a bypass line in order to measure the influent PCE concentration. When a steady state was reached, the flow was directed to the reactor, and the furnace temperature was ramped to the desired final temperature at 2 °C/min. As discussed later, the apparent first-order reaction rate constants (Table 2) for reduction and oxidation of PCE were such that reaction characteristic times (inverse of the rate constant) were of the order of seconds. Due to the relatively slow rate of temperature change, the reactor was assumed to operate at steady state for any given temperature. The effluent gas stream was periodically sampled and analyzed. At the end of the experiment, all gas streams were turned off except for O₂, and the furnace temperature was held at 450 °C for 8 h in order to clean the catalyst surface. This process proved to be effective in maintaining the catalyst performance characteristics for over 2 years.

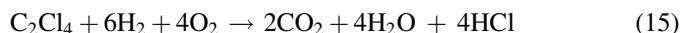
3. Results and discussion

Multiple reduction and oxidation reactions are anticipated in this complex reaction system. Since the major end products are CO₂, H₂O and HCl (and/or Cl₂), relevant reaction pathways

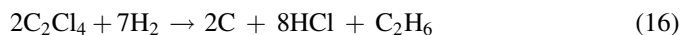
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Since the contribution of each reaction pathway depends on the initial reactant composition and the reaction temperature, a combined reaction equation can take various forms, such as:



In addition, carbonaceous material (coke) may be produced and some intermediate products may be further converted, as illustrated below and discussed later:



When H₂ and O₂ are present in the system simultaneously, H₂ can be oxidized exothermically by O₂ (Eq. (13)) with an enthalpy change of −241.8 kJ/mol H₂. In our system, this reaction acts as an internal heater, generating a temperature difference between the furnace and the catalyst surface. The measured temperature difference increased with the H₂/O₂ ratio in the feed, as seen in Fig. 2. In particular, at H₂/O₂ = 2.15, the catalyst surface became hotter than the furnace by about 100 °C. In all cases, the temperature difference between the furnace and the catalyst surface started to occur at approximately 100 °C. From 100 to 140 °C, the catalyst surface temperature increased much more rapidly than the furnace temperature. At higher temperatures, the catalyst surface was hotter than the furnace by a fixed value (for a given H₂/O₂).

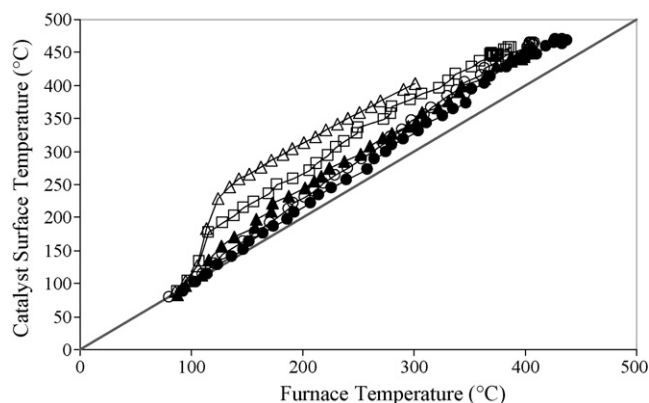


Fig. 2. Catalyst surface temperature as a function of furnace temperature at different H₂/O₂ ratios. O₂ was 5% by volume in the feed, and H₂ was varied to achieve the respective H₂/O₂ ratios. Gas flow rate: 500 mL/min (at 25 °C). Legend: (Δ) H₂/O₂ = 2.15, (□) H₂/O₂ = 1.18, (▲) H₂/O₂ = 0.67, (○) H₂/O₂ = 0.26, (●) H₂/O₂ = 0. The solid straight line corresponds to slope = 1.

Table 2

The apparent first-order rate constant for oxidization and reduction of PCE

Temperature (°C)	Oxidation (H ₂ -free) <i>k</i> (1/s)	Reduction (O ₂ -free) <i>k</i> (1/s)
200		1.04
250		1.37
300		2.39
400	0.08	
450	0.29	
488	0.53	

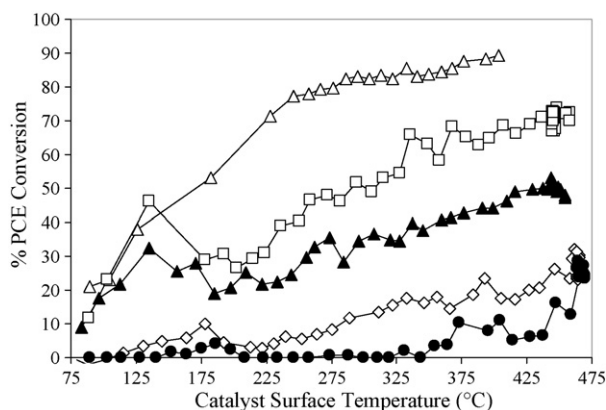


Fig. 3. PCE conversions at different H_2/O_2 ratios. O_2 was 5% by volume in the feed, and H_2 was varied to achieve the respective H_2/O_2 ratios. PCE concentration in the influent stream was 800 ppmv. Gas flow rate: 500 mL/min (at 25 °C). Legend: (Δ) $H_2/O_2 = 2.15$, (\square) $H_2/O_2 = 1.18$, (\blacktriangle) $H_2/O_2 = 0.67$, (\diamond) $H_2/O_2 = 0.26$, (\bullet) $H_2/O_2 = 0$.

3.1. Effect of H_2/O_2 ratio and temperature on PCE conversion

The catalytic destruction of PCE was studied as a function of H_2/O_2 ratio and catalyst surface temperature. The percent conversion of PCE versus temperature for H_2/O_2 molar ratios ranging from 0 to 2.15 is shown in Fig. 3. The percent conversion of PCE was calculated from:

$$\% \text{PCE conversion} = 100 \times \left(1 - \frac{C_{\text{out}}}{C_{\text{in}}} \right) \quad (19)$$

where C_{in} and C_{out} are the influent and effluent PCE concentrations (mol/L), both measured at room temperature.

At any given temperature, the conversion of PCE generally increased with increasing H_2/O_2 (Fig. 3). At any given H_2/O_2 ratio, the conversion of PCE also generally increased with increasing temperature, with some exceptions in the range of 130–200 °C (which will be discussed further in Section 3.2). At the highest H_2/O_2 ratio of 2.15, which is slightly greater than the stoichiometric H_2 -to- O_2 ratio for the production of water (Eq. (13)), PCE conversion increased steadily with increasing temperature, reaching about 90% at 400 °C. At higher temperatures, no PCE was detected in the effluent (detection limit about 1 ppmv). In the H_2 -free experiments ($H_2/O_2 = 0$), PCE removal was observed only at $T > 350$ °C, and PCE conversion was lower than in the presence of H_2 . For example, at 450 °C, PCE conversion was only about 15%. We are not aware of other studies on H_2 -free PCE oxidation on similar catalysts, but the trend and the conversion efficiencies here are similar to TCE oxidation on a similar catalyst [8,11]. On the other hand, purely reductive conditions (i.e., O_2 free) resulted in rapid catalyst deactivation, which will be discussed further in Section 3.2. Overall, Fig. 3 indicates that PCE conversion was sensitive to H_2/O_2 ratio and reactor temperature. Clearly, PCE conversion was favored by $T \geq 400$ °C and $H_2/O_2 = 2.15$. These observations are consistent with recent studies in our laboratory on catalytic dechlorination of other compounds [56].

At any temperature, conversion increased as H_2/O_2 increased for TCE and chloroform on 0.5% (w/w) Pt/ γ - Al_2O_3 . For example, at 60 °C and $H_2/O_2 = 0.3$, TCE conversion was 30% but increased to 89% for $H_2/O_2 = 3$. In a parallel experiment, chloroform conversion increased from 0 to 20%. TCE conversions also increased with temperature (e.g., from 84% at 22 °C to 95% at 100 °C) on 0.5% (w/w) Pt/ γ - Al_2O_3 [56]. In all these experiments, the residence times were comparable to those in this study.

3.2. Catalyst deactivation

The effect of H_2/O_2 ratio on PCE conversion is ultimately related to the mechanism of catalyst deactivation, which is currently being debated in the literature. As mentioned earlier, catalyst deactivation during gas-phase HDC has been linked to several physicochemical phenomena. While HCl was proposed as a primary cause of deactivation for Ni [57], noble metals [27,29,58], and metal sulfides [59], it did not appear to cause deactivation for certain alumina and Pt/alumina catalysts [49,60]. There is no systematic understanding yet on how Cl_2 , HCl, and surface chloride (or their synergistic effects) cause the deactivation of various catalysts. Other proposed causes of deactivation include metal particle sintering [61] and coke deposition [62,63]. Based on the relevant reactions discussed earlier, we shall focus on coke formation and chlorine poisoning as the major mechanisms of catalyst deactivation.

Reduction of PCE by H_2 is relatively fast, and the end products (e.g., C_2H_6 , HCl) are less environmentally hazardous than those obtained from PCE oxidation (e.g., Cl_2 , as well as furans and dioxins). However, under reducing-only conditions, catalyst deactivation is a major problem. H_2 -only experiments were carried out at two temperatures, 180 °C and 280 °C (Table 3). In both cases, PCE conversion decreased substantially over periods of minutes to hours. Physicochemically, adsorption of certain PCE reduction intermediates (mainly coke) on the catalyst surface would occupy active sites and compete with other reactants. On the other hand, PCE oxidation produces Cl_2 , which can also poison catalysts by occupying active sites. O_2 -only experiments were carried out at two temperatures, 380 °C and 450 °C (Table 3). Sustained conversions were observed for several hours, which indicates a much slower deactivation under the purely oxidative condition than the reductive one. This is consistent with some previous observations on similar noble metal/alumina catalysts, e.g. [64].

In principle, the poisonous intermediates from reduction alone can be removed via oxidation to CO_2 . Intermediates from oxidation, such as Cl_2 , can be converted to compounds (such as HCl) that are more easily removable from the catalyst in the effluent stream, if a hydrogen source (such as H_2) is present. In our “redox” reaction system, with both H_2 and O_2 present, high PCE conversions were achieved for extended periods at temperatures lower than those under reduction or oxidation alone (Table 3). At 180 °C, 280 °C and 450 °C, PCE conversion was 67%, 72% and 84%, respectively, for more than a few hours under the mixed redox conditions. In practice, the same catalyst

Table 3

Observations on time dependence of catalyst activity under H₂-only, O₂-only and redox conditions

	<i>T</i> = 180 °C	<i>T</i> = 280 °C	<i>T</i> = 380 °C	<i>T</i> = 450 °C
H ₂ -only (6%)	Conversion decreased from 15% to zero in 30 min	Conversion decreased from 98 to 38% in 1 h 50 min		
O ₂ -only (5%)			Conversion was ~30% for 4 h	Conversion was ~30% for 4 h
Redox (6% H ₂ , 3% O ₂)	Conversion was steady at 67% for 5 h 30 min	Conversion was steady at 72% for 2 h		Conversion was steady at 84% for 30 h

Other experimental parameters are the same as in Fig. 3.

was used under “redox” without apparent deactivation for over 2 years. PCE conversion produced primarily CO₂, H₂O, HCl (Eq. (15)) and ethane (Eqs. (10) and (16)). No partially dechlorinated hydrocarbons were detected by GC-FID (detection limits about 0.5–1 ppmv for short-chained chlorinated alkanes and alkenes).

A close examination of Fig. 3 shows that PCE conversion decreased slightly as temperature was ramped through the range 130–200 °C, for all the H₂/O₂ ratios except for the H₂/O₂ = 2.15 case. This can be explained by the catalyst deactivation scenarios discussed above. Initially (*T* < 130 °C), PCE conversion occurred readily on a clean catalyst surface. At relatively low temperatures, however, the catalyst surface was gradually occupied by intermediate products (mostly coke from reduction and possibly chlorine species from oxidation) that could block active sites and limit PCE adsorption, leading to catalyst deactivation and the drop in PCE conversion efficiency. As temperatures rose (apparently above ~200 °C), accumulated organic (and chlorine) species were volatilized and/or destroyed by reactions with O₂, thereby freeing available catalyst sites. The main oxidation products were CO₂ and water vapor, neither of which is prone to adsorption. As a result, PCE conversion increased again. This “self-cleaning” process regenerated the catalyst by effectively reversing deactivation. On the other hand, at H₂/O₂ = 2.15, the surface temperature rose so rapidly (mainly due to Reaction (13)) that coke deposition and catalyst deactivation were prevented entirely or were not noticeable due to the relatively high PCE conversions. By comparison, at lower H₂/O₂ ratios, the catalyst temperature did not rise fast enough to prevent deactivation (Fig. 2).

At this point, the microscopic details of catalyst deactivation and recovery as well as the reaction mechanisms involved cannot be fully elucidated until further experiments are carried out. However, it is worthy to pursue if water, which was evidently produced in the course of our redox experiments, plays a role in PCE conversion. Previous work has suggested that in certain systems (such as TCE oxidation), water may enhance the conversion efficiency of chlorinated compounds under certain conditions [11]. In the cases in Fig. 3 where H₂/O₂ ratios were 0.26, 0.67 and 1.18, if H₂ were quickly consumed by O₂ to produce water, thus preventing H₂ from reacting with PCE, then water would have to be mainly responsible for the observed PCE conversions that are higher than in the O₂-only case (lowest curve in Fig. 3). However, our experiments show that this was apparently not the case. When water vapor (0.4% and 2.4%) was mixed with 800 ppm PCE and ~5% O₂ in the

influent stream, both water/O₂ and the O₂-only conversion curves overlap and are far beneath any of the H₂/O₂ curves (results not shown). In particular, this indicates that the substantial conversions observed in the presence of H₂ at low temperatures (130–200 °C) cannot be due to the effect of water alone. Since conversions due to oxidation do not occur until 350 °C, it is most likely that reduction by H₂ was the main mechanism for these low-temperature conversions. We note, however, that it would be premature to rule out any beneficial effects of water on PCE conversion. For example, water may help remove HCl from the catalyst, thus reducing catalyst deactivation and improving PCE conversion. This may also be part of the reason why the catalyst started its recovery from deactivation before the temperature was high enough for efficient PCE oxidation (*T* > 350 °C). Such a mechanism has been reported in other HDC systems. For example, Noelke and Rase [65] found that continuous addition of water vapor more than doubled the rate of chloroform HDC on a commercial Pt/Al₂O₃ catalyst by removing chlorine from the alumina.

To examine the effect of excess H₂ on PCE conversion, an experiment was conducted at H₂/O₂ = 4.6 (Fig. 4). Initially, PCE was efficiently converted (80% at 75 °C, compared to 21% at 89 °C for H₂/O₂ = 2.15). Excess hydrogen may reduce PCE at lower temperatures and/or overcome competition from O₂ for the catalyst's active sites. At higher temperatures (until ~200 °C), conversion of PCE decreased slightly in the H₂/O₂ = 4.6 case but increased in the H₂/O₂ = 2.15 case until the two conversions became indistinguishable. In the first case, the minor loss of PCE conversion efficiency may have arisen from

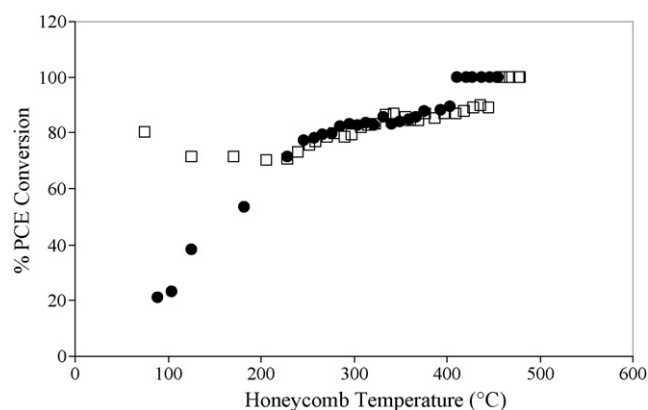


Fig. 4. Effect of excess hydrogen on the conversion of PCE. O₂ was 5% by volume in the feed. Gas flow rate: 500 mL/min (at 25 °C). Legend: (□) H₂/O₂ = 4.6, (●) H₂/O₂ = 2.15.

rapid catalyst coking under a mainly reducing condition. At temperatures above 200 °C, the self-cleaning process that was effective at lower-H₂ levels was also effective in the higher-H₂ case. A more detailed mechanistic explanation can be provided after the effluent gas composition (products and residual H₂ and O₂) is completely determined. PCE was below the detection limit in the reactor effluent at $T > 412$ °C for H₂/O₂ = 2.15 and at $T > 446$ °C for H₂/O₂ = 4.6. Apparently, excess H₂ did not improve PCE conversion at higher reactor temperatures. It is evident that the simultaneous presence of H₂ and O₂ at a 2:1 molar ratio effectively prevents catalyst poisoning, leading to efficient, long-term PCE conversion.

3.3. Reaction kinetics

Although previous work suggests that the dependence of HDC rate on reactant concentrations is complex, a pseudo-first order relationship provides a reasonable approximation for both olefinic (e.g., PCE, TCE, and DCE isomers) and aromatic (e.g., chlorobenzene) systems [22,46,66]. In this study, only strictly oxidizing (oxygen, nitrogen and PCE, but no hydrogen) or reducing (hydrogen, nitrogen and PCE, but no oxygen) condition was examined at first to investigate the kinetics of PCE destruction via oxidation or reduction alone, without possible complications introduced by the simultaneous presence of either multiple reaction pathways or multiple reactants and products that may compete for adsorption sites on the catalyst surface. Reaction order with respect to PCE concentration was investigated by systematically varying the nominal reactor residence time while maintaining the influent PCE, H₂ and O₂ concentrations constant. Apparent first-order dependence of reaction rate on PCE concentration under isothermal and plug-flow conditions yields:

$$C_{\text{out}} = C_{\text{in}} \exp(-k\theta) \quad (20)$$

where θ is the residence time in the reactor(s), $\theta = V/Q$ where Q is the volumetric flow rate at the honeycomb temperature (L/s) and V is the honeycomb pore volume (L); k is the apparent first-order rate constant for PCE destruction (1/s).

Since O₂-free experiments lead to catalyst deactivation, the reactor temperature was raised to 450 °C and purged with a mixture of oxygen and nitrogen for 4 h at the end of each experiment. Such treatment effectively cleaned the catalyst, restoring the original catalytic reactivity for the next experiment. Under either oxidizing or reducing condition, first-order apparent rates were observed at each of the three temperatures studied (Fig. 5). In the absence of O₂, the apparent rate constant for PCE conversion increased with temperature in the range 200–300 °C (Table 2). A similar trend was observed in the H₂-free experiments, although the temperature range was necessarily higher. We note that since the whole catalyst was not equally active, these apparent rate constants are probably lower-limit values. It is evident that PCE reduction was much faster and proceeded at much lower temperatures than PCE oxidation (Table 2). This has implications for the mixed reaction scheme with both H₂ and O₂. It is likely that PCE reduction steps precede oxidation

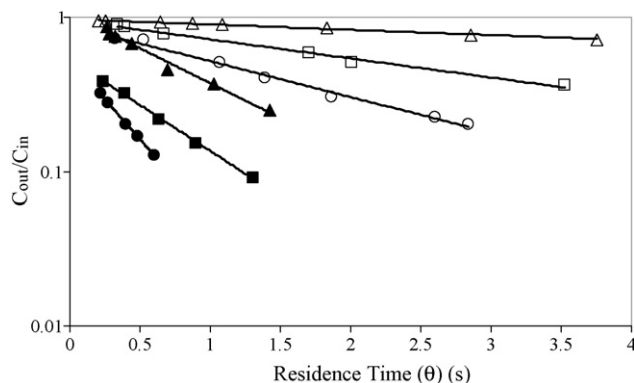


Fig. 5. Kinetics of oxidation (H₂-free, open symbols, 5% O₂ in the feed) and reduction (O₂-free, filled symbols, 5% H₂ in the feed) of PCE at various temperatures: (▲) 200 °C, (■) 250 °C, (●) 300 °C, (◈) 400 °C, (□) 450 °C, (○) 488 °C. Solid lines are exponential fits.

reactions and that the importance of oxidation lies in its elimination of intermediates that would otherwise quickly poison the catalyst.

The exponential regression of the lines in Fig. 5 should all go to $C_{\text{out}}/C_{\text{in}} = 1$ at $V/Q = 0$. This is not always the case. There is no conclusive explanation for this apparent discrepancy, which is most pronounced for the relatively fast PCE transformations at high temperatures under the O₂-free condition. Note that the residence times under these conditions were also relatively short. It is possible that actual residence times were slightly longer than the calculated nominal residence times, which could arise from measurement errors. Only a small displacement of the regression lines for the high-temperature, reducing-condition data would be needed to eliminate the apparent discrepancy.

The apparent activation energy for PCE conversion under either reduction or oxidation condition was calculated using the Arrhenius equation:

$$k = k_0 \exp\left(-\frac{E_a}{RT}\right) \quad (21)$$

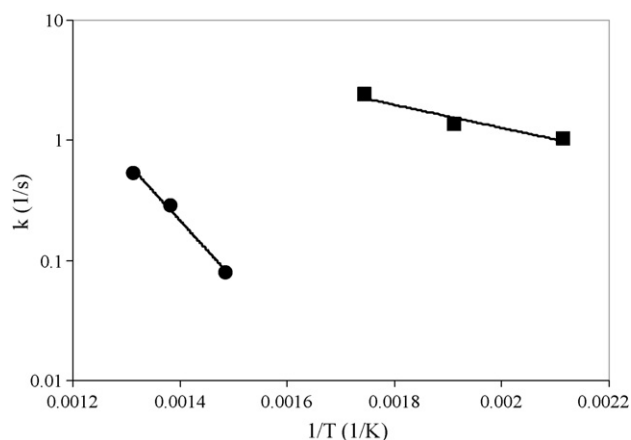


Fig. 6. Arrhenius plot of apparent first-order rate constants (obtained from Fig. 5) for oxidation (H₂-free, ●) and reduction (O₂-free, ■) of PCE. Solid lines are fits of Eq. (21). Fitting parameters yield, for oxidation: $k_0 = 1.46 \times 10^6 \text{ s}^{-1}$, $E_a = 93.4 \text{ kJ/mol}$, and for reduction: $k_0 = 107 \text{ s}^{-1}$, $E_a = 18.4 \text{ kJ/mol}$.

where E_a is the apparent activation energy (J mol^{-1}), k_0 is the pre-exponential factor (s^{-1}) and R is the gas constant ($8.31 \text{ J mol}^{-1} \text{ K}^{-1}$). Results are shown in Fig. 6. The apparent activation energies for PCE reduction and oxidation are found to be 18.4 and 93.4 kJ/mol, respectively. In comparison, Ordoñez et al. [63] reported an activation energy for the HDC of PCE as 26.7 kJ/mol using a 0.5% Pd/alumina catalyst. Kim and Allen [46] reported an activation energy for the HDC of PCE as approximately 50 kJ/mol on a commercial NiMo/ Al_2O_3 catalyst under high pressure (about 100 atm). However, we are not aware of other studies on PCE HDC using the Pt/Rh catalyst employed in this work. It is important to point out that the apparent values of E_a reported might be affected by possible variations of adsorption equilibria with temperature for PCE, other reactants (H_2 or O_2) and even reaction products.

The relatively low value found for the activation energy under the reducing condition could suggest that mass transfer limitations are playing a role in the apparent reaction rates. The main mass transfer limitation would be the transport of reactants from the gas phase to the catalyst surface. Within each channel of the honeycomb, if we assume that mass transfer is exclusively due to diffusion (which would overestimate mass transfer limitations), a characteristic time for the transport of PCE from the gas to the solid surface is $t_m \sim \delta^2/D_p$, where δ is the diffusion distance ($\sim 1 \text{ mm}$) and D_p is the diffusivity of reactant (e.g. PCE) in the gas. Taking $D_p \sim 0.1 \text{ cm}^2/\text{s}$, we find $t_m \sim 0.1 \text{ s}$. The highest apparent reaction rate constant measured in this work was on the order of 2.5 s^{-1} . This yields a reaction characteristic time of $\sim 0.4 \text{ s}$. We can see that, even under extreme conditions, mass transfer is appreciably faster than the reaction, which indicates that mass transfer limitations are not important under the experimental conditions.

It is evident from the results in Fig. 3 that the conversion of PCE depends, at least partially, on hydrogen concentration. First-order apparent kinetics would be a result of excess hydrogen for the PCE reduction reaction. A simple kinetic model for PCE reduction would be to consider that the reaction is also first order with respect to hydrogen concentration. If this is the case, then the pre-exponential factor of the apparent first-order constant would be:

$$k_0 = k'_0 C_H \quad (22)$$

where C_H is the hydrogen concentration in the gas and k'_0 is the pre-exponential factor of PCE/ H_2 reaction rate constant that is independent of H_2 concentration. If we assume that, in the presence of hydrogen, the reduction reaction dominates, and that the kinetics varies with hydrogen concentration as represented by Eq. (22), then we should be able to predict the results under the experimental conditions in Fig. 3 using the k'_0 and E_a for reduction obtained in Fig. 6, which is an independent experiment. The only additional aspect to consider in the analysis of the data in Fig. 3 is that, since the volumetric flow rate of gas was kept constant at 500 mL/min measured at ambient temperature ($T_a = 298 \text{ K}$), the residence time in the reactor would change with temperature due to gas expansion. The residence time calculated at ambient temperature is

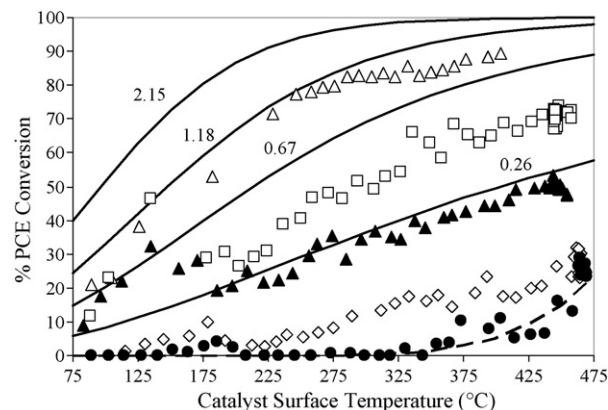


Fig. 7. Prediction of PCE conversions using the parameters in Fig. 6 and the procedure outlined in the text for: pure oxidation (dashed line), and pure reduction (solid lines; numbers next to lines represent respective H_2/O_2 ratios for calculated conversions). Caption as in Fig. 3.

$\theta_0 = 1.5 \text{ s}$, so that:

$$\theta = \theta_0 \frac{T_a}{T} \quad (23)$$

Fig. 7 shows the predictions (solid lines), along with a calculation for pure oxidation based on the parameters reported in Fig. 6 (dashed line). Note that, as expected, the pure oxidation curve accurately predicts the experimental results in the absence of hydrogen. However, the predictions for the mixed H_2/O_2 cases overestimate the conversions determined experimentally. The inadequacy of this model indicates that it is probably too simple to represent the process. If partial deactivation of the catalyst occurs or if competition for active sites by O_2 , whose presence is necessary to maintain catalyst activity, plays a role in the kinetics of the mixed redox system, the model would change substantially. In addition, the possible competition from parallel processes, such as adsorption/desorption rates and parallel reactions such as oxidation of H_2 to form water, would need to be considered in a more rigorous formulation. More research is needed to determine the mechanistic aspects of the process, including the rate-determining steps in the conversion of PCE.

4. Conclusions

The simultaneous presence of hydrogen and oxygen (mixed redox conditions) at a 2:1 molar ratio yields an optimum operating environment for the destruction of PCE over a Pt/Rh on Al_2O_3 catalyst. Results suggest that the redox conditions allow for high conversions at relatively low temperatures mainly through a reductive dehalogenation reaction pathway, while the presence of oxygen prevents catalyst deactivation. Detailed mechanistic studies are necessary to elucidate the role of oxygen in maintaining catalyst stability. We have successfully implemented this unique method in a pilot field study, using propane as the alternative reductant. This will be reported in an upcoming paper.

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